

RESPONSE UNDER 37 CFR § 1.116  
Appln. No. 09/924,546

**REMARKS**

In the Office Action of March 1, 2004 (January 5, 2004) claims 1, 3, and 5-16 were rejected under 35 U.S.C. § 112, second paragraph, as allegedly being indefinite with respect to the claim terminology “non-woven fabric”, based on the Examiner’s indication that such should be defined based on structural and/or chemical characteristics rather than the physical properties thereof. Claims 1, 3, and 5-16 were rejected under 35 U.S.C. § 103(a) based on Aikawa et al. (U.S. Patent 6,284,680) in view of Ohta et al (U.S. Patent 6,605,348). Lastly, claims “1-16” (sic) were rejected for obviousness-type double patenting based on claims 1-6 of U.S. Patent 6,284,680 (Aikawa et al) in view of Ohta et al (U.S. Patent 6,605,348).

Preliminarily, before addressing the details of the Office Action, for the Examiner’s background information, the undersigned has been advised that with respect to the 3 Japanese patent applications identified on the cover page of Aikawa et al U.S. Patent 6,284,680, the first and third were not published, because they were claimed under the Japanese domestic priority system in a later application. With respect to the second identified Japanese patent application, viz., Japanese Patent Application No. 10-339858, such was published on June 13, 2000, as Publication No. 2000-160432 (a copy and English Abstract of which were submitted with the Information Disclosure Statement and Form PTO-1449 filed on November 9, 2001).

In response, with respect to the remaining § 112 rejection, in the previous Amendment, independent claim 1 was amended to further describe the physical characteristics of the non-woven fabric with respect to fibers thereof and their properties. A recitation of further structural

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and/or chemical characteristics of the non-woven fabric are not required by § 112. In that regard, see claim 1 of the Aikawa et al reference, which, like claim 1 of the present application, recites physical characteristics of the fabric and the fibers forming the fabric, and does not include further structural or chemical characteristics.

Therefore, unless the very nature of the invention resides in the chemical composition, a further limitation regarding the chemical composition of fibers forming the non-woven fabric is unnecessary. It is noted, though, for the Examiner's information, that in the case of a preferred embodiment of the present invention, as set forth in claim 10, the non-woven fabric is defined as consisting essentially of polyolefin-based fibers.

With respect to the § 103(a) rejection of claims 1, 3, and 5-16 based on Aikawa et al (U.S. Patent 6,284,680) in view of Ohta et al (U.S. Patent 6,605,348), it first is noted that even if the Aikawa et al reference might be considered to constitute prior art under 35 U.S.C. § 102(e), this does preclude patentability under 35 U.S.C. § 103(a), in view of the provisions of 35 U.S.C. § 103(c). Particularly, in this regard, it is noted that Aikawa et al (U.S. Patent 6,284,680) and the present invention have been and are owned by the same entity or subject to an obligation of assignment to the same entity (Japan Vilene Co. Ltd.) at the time the invention was made.

Accordingly, it is respectfully submitted that the rejection under 35 U.S.C. § 103(a) based on Aikawa et al in view of Ohta et al should be withdrawn.

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In addition to the foregoing, Applicants also submit herewith a Certificate of Verification with an attached English language translation of Japanese Patent Application JPA No. 2000-243230 filed 8/10/2000) in support of Applicants' claim to the benefit of the priority date of Japanese Patent Application No. 2000-243230. This precedes the effective date (April 4, 2001) of Ohta et al's U.S. Patent 6,605,348 as a reference. Therefore, the § 103(a) rejection based on Ohta et al should be withdrawn for this reason also.

Lastly, with respect to the obviousness-type double patenting rejection of claims 1-16 based on claims 1-6 of U.S. Patent 6,284,680 (Aikawa et al) in view of Ohta et al (U.S. Patent 6,605,348), Applicants respectfully traverse.

In support of the obviousness-type double patenting rejection, the Examiner, although recognizing that the alleged conflicting claims are not identical, asserted that these are obvious variants, since, in the Examiner's opinion, the only apparent difference was in the preamble "batteries separator", and the Examiner considered the Ohta et al reference to describe modulus characteristics.

However, as noted above, in view of the submission herewith of the Verified translation of JPA No. 2000-243230 supporting Applicants' claimed priority date of August 10, 2000, Ohta et al U.S. Patent 6,605,348 is no longer proper as a basis for rejection of the claims of the

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present application, and for this reason, *inter alia*, the obviousness-type double patenting rejection should be withdrawn.

In view of the above, reconsideration and allowance of pending claims 1, 3, and 5-16 of this application are now believed to be in order, and such actions are hereby solicited.

If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned attorney at the Washington, D.C. telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

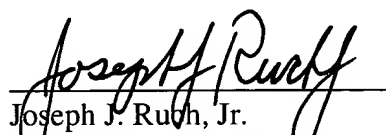
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WASHINGTON OFFICE

**23373**

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## CERTIFICATE OF VERIFICATION

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of c/o Morita & Associates, 5th Fl., Itabashi-Chuo Bldg.,  
67-8, Itabashi 2-chome, Itabashi-ku, Tokyo 173-0004, Japan,  
state that the attached document is a true and complete  
translation to the best of my knowledge of Japanese Patent  
Application No. 2000-243230.

Dated this 22nd day of March, 2004

Signature of translator: M. Harabayashi



JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of  
the following application as filed with this Office.

Date of Application: August 10, 2000  
Application Number: Japanese Patent Application  
No. 2000-243230  
Applicant(s): Japan Vilene Co., Ltd.

June 27, 2001

Commissioner,  
Japan Patent Office      Kozo OIKAWA

Certificate Issuance No. 2001-3060447

[DOCUMENT NAME] Patent Application  
[REFERENCE NUMBER] PJV00-038A  
[ADDRESSEE] Director-General of Patent Office  
[INTERNATIONAL PATENT CLASSIFICATION] H01M 2/14  
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[INDICATION OF FEE]

[Deposit Account Number] 055583

[Fee] 21,000

[LIST OF SUBMITTED DOCUMENTS]

[Name of Document]	Specification	1
[Name of Document]	Abstract	1
[REQUEST FOR PROOF]	YES	



[DOCUMENT NAME] Specification

[TITLE OF THE INVENTIONS] BATTERY SEPARATOR

[CLAIMS]

[Claim 1] A battery separator, characterized by consisting of a nonwoven fabric having a substantially unilayered structure, wherein an apparent total surface area of fibers per a unit area of said nonwoven fabric is  $20 \text{ m}^2/\text{m}^2$  or more, and a thickness of said nonwoven fabric is 0.1 mm or less.

[Claim 2] The battery separator according to claim 1, characterized in that the nonwoven fabric consists of non-fibrillated fibers.

[Claim 3] The battery separator according to claim 1 or 2, characterized in that the nonwoven fabric contains high-modulus fibers having a Young's modulus of 50 cN/dtex or more.

[Claim 4] The battery separator according to any one of claims 1 to 3, characterized in that the nonwoven fabric contains fine fibers having a fiber diameter of 4  $\mu\text{m}$  or less.

[Claim 5] The battery separator according to any one of claims 1 to 4, characterized in that the nonwoven fabric consists essentially of polyolefin-based fibers.

[Claim 6] The battery separator according to any one of claims 1 to 5, characterized in that the fibers forming the nonwoven fabric are fixed substantially only by fusing the fibers to each other.

[Claim 7] The battery separator according to any one of claims 1 to 6, characterized in that a uniformity index of said nonwoven fabric is 0.15 or less.

[Claim 8] The battery separator according to any one of claims 1 to 7, characterized in that a maximum pore size in

the nonwoven fabric is 40  $\mu\text{m}$  or less.

[Claim 9] The battery separator according to any one of claims 1 to 8, characterized in that a void rate of the nonwoven fabric is 45 to 65 %.

[Claim 10] The battery separator according to any one of claims 1 to 9, characterized in that a tensile strength of the nonwoven fabric in at least one direction is 20 N/5cm width or more.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to which the Invention Pertains]

The present invention relates to a battery separator.

[0002]

[Prior Art]

In an alkaline battery, a separator is used to separate a positive electrode and a negative electrode from each other to prevent a short circuit therebetween, and further, to hold an electrolyte thereon and enable a smooth electromotive reaction.

[0003]

Recently, in electronic equipment, a space allotted for the battery has become smaller due to the need for miniaturization and weight-saving. Nevertheless, the performance requirement for such a smaller battery is the same as or higher than that for a conventional battery, and therefore, it is necessary to enhance the capacity of the battery, and to increase the amounts of active materials in the electrodes. Accordingly, a volume allotted in the battery for the separator must be reduced. Although the present applicant proposed a separator having a thickness of 1.5 mm, a thinner separator having a thickness of 1.0 mm or less is desired in the market.

[0004]

A separator having such a thickness is proposed in Japanese Unexamined Patent Publication (Kokai) No. 11-126595. This Publication discloses an alkaline battery separator having a mass per unit area of 15 to 55 g/m<sup>2</sup>, a void rate of 40 to 80 %, and a thickness of 0.05 to 0.12 mm, and composed of a laminated nonwoven fabric prepared by adhering fine-fiber nonwoven fabrics onto both sides of a nonwoven fabric produced by a wet-laid method and containing sheath-core type composite fibers consisting of a sheath polymer with a low melting point and a core polymer with a high melting point.

[0005]

[Problems to be Solved by the Invention]

However, the separator is composed of the laminated nonwoven fabric prepared by adhering fine-fiber nonwoven fabrics and the nonwoven fabric produced by a wet-laid method, and thus, the electrolyte is unevenly distributed at the fine-fiber nonwoven fabrics. Therefore, an inner pressure is increased, and as a result, it becomes difficult to enhance the capacity of the battery, although the separator is designed to be thinner to enable an enhancement of the capacity of the battery.

The object of the present invention is to remedy the above disadvantages of the prior art and provide a thin battery separator enabling an enhancement of the capacity of the battery.

[0006]

[Means for Solving the Problems]

In accordance with the present invention, there is provided a separator for an alkaline battery (hereinafter sometimes referred to as "separator" simply), characterized

by consisting of a nonwoven fabric having a substantially unilayered structure, wherein an apparent total surface area of the fibers per a unit area of the nonwoven fabric is  $20 \text{ m}^2/\text{m}^2$  or more, and a thickness of the nonwoven fabric is 0.1 mm or less.

As the separator of the present invention has a substantially unilayered structure, an electrolyte can be evenly held throughout the nonwoven fabric, and therefore, a battery having a low inner pressure and a high capacity can be assembled. Further, the nonwoven fabric has the apparent total surface area of the fibers per a unit area of  $20 \text{ m}^2/\text{m}^2$  or more, even though the thickness is as thin as 0.1 mm or less. Therefore, a battery having a good electrolyte-holding capacity (particularly, a long-term electrolyte-holding capacity) and a long-term lifetime, can be assembled.

[0007]

[Mode for Carrying out the Invention]

The separator of the present invention has a substantially unilayered structure, to avoid an uneven distribution of electrolyte. The expression "substantially unilayered structure" as used herein means that an average fiber diameter of fibers contained in the separator does not vary (within  $\pm 20\%$ ) in a direction of the thickness of the separator. When two fiber sheets are laminated when preparing a separator, and each average fiber diameter of fibers containing each fiber sheet is the same (within  $\pm 20\%$ ), the separator is deemed a separator having a substantially unilayered structure.

The term "direction of the thickness" or "thickness direction" as used herein means a direction at a right angle to a surface of a plate, when the plate (20 g per 1

cm<sup>2</sup>) is mounted on a separator. The term "average fiber diameter" as used herein with respect to short fibers means an average of fiber diameters of 100 or more short fibers. The term "average fiber diameter" as used herein with respect to long fibers means an average of fiber diameters of 100 or more points of long fibers. The term "fiber diameter" as used herein with respect to a fiber having a circular cross-sectional shape means a diameter of the circle. For a fiber having a non-circular cross-sectional shape, a diameter of a circle having an area the same as that of the non-circular cross-sectional shape is regarded as a diameter.

[0008]

The fibers forming the separator of the present invention are not particularly limited, but it is preferable that the separator consists of non-fibrillated fibers. When the separator consists of non-fibrillated fibers, the uniformity of the separator becomes uniform, and an electrolyte can be evenly held throughout the whole separator.

The expression "non-fibrillated fiber" as used herein means a fiber without a binding portion of plural fibers. A fiber that is not the "non-fibrillated fiber" is, for example, a fiber having many branches divided therefrom (for example, fibers prepared by beating mechanically dividable fibers by a beater, or pulp), or fibers having a network structure formed by binding plural fibers to each other (for example, fibers obtained by a flush spinning method).

[0009]

The separator of the present invention may be formed from one or more materials, such as polyamide-based fibers,

polyolefin-based fibers, or the like. It is preferable that the nonwoven fabric consists essentially of polyolefin-based fibers, because such fibers exhibit an excellent resistance to an electrolyte, and do not generate the ammonia that is believed to be a cause of self-discharging. The fiber consisting "essentially" of a polyolefin-based resin (polyolefin-based fiber) means a fiber of which the surface is formed by a polyolefin-based resin. This is because a part having an influence on the resistance to an electrolyte is the surface of the fiber. For example, a composite fiber composed of a polyamide resin and a polyolefin resin, and having a surface consisting of polyolefin-based resin is included in the above polyolefin-based fiber.

[0010]

As the polyolefin-based resin, there may be mentioned, for example, polyethylene-based resins, such as, ultra-high-molecular-weight polyethylene, high-density polyethylene, middle-density polyethylene, low-density polyethylene, linear low-density polyethylene, or ethylene copolymers, polypropylene-based resin, such as polypropylene, propylene copolymers, or polymethylpentene-based resin, such as polymethylpentene, methylpentene copolymers. Of these resins, polypropylene-based resin or polyethylene-based resin is preferable.

[0011]

When the separator of the present invention contains high-modulus fibers having a Young's modulus of 50 cN/dtex or more, because of the elasticity of the high-modulus fibers, a short circuit caused by a penetration into the separator by a flash generated at the electrode is avoided, and the separator is prevented from being torn by an edge

of an electrode, when the separator is wrapped around the electrodes. Therefore, a battery can be reliably assembled.

Further, moderate voids are maintained in the separator after wrapping the electrodes, and an electrolyte can be held for a long time. Therefore, a battery having a long lifetime can be assembled.

The term "Young's modulus" as used herein means an apparent Young's modulus calculated from an initial tensile strength determined in accordance with a method defined in JIS (Japanese Industrial Standard) L 1015:1999, 8.11. The initial tensile strength is determined by a tester of a constant rate of strain type.

The above advantageous effects can be obtained from a higher Young's modulus. The Young's modulus is preferably 65 cN/dtex or more, more preferably 80 cN/dtex or more.

The above advantageous effects may be easily achieved if the high-modulus fibers are contained at an amount of 5 mass% or more, preferably 10 mass% or more, in the fibers forming the separator. On the other hand, it is preferable that the amount of the high-modulus fibers is 60 mass% or less, because it is preferable to contain an appropriate amount of fine fibers to enhance the electrolyte-holding capacity.

A material for the high-modulus fibers may be, for example, polyethylene-based resins, such as, ultra-high-molecular-weight polyethylene, high-density polyethylene, middle-density polyethylene, low-density polyethylene, linear low-density polyethylene, or ethylene copolymers, polypropylene-base resin, such as high-crystalline polypropylene, propylene copolymers, or polymethylpentene-based resin, such as polymethylpentene, methylpentene

copolymers. Of these resins, ultra-high-molecular-weight polyethylene or high-crystalline polypropylene is preferable.

The high-modulus fiber used in the present invention may be composed of a single component of the above material, or a mixture or a composite of two or more components of the above materials. When the high-modulus fiber is a composite fiber composed of two or more materials as above, the cross-sectional shape may be, for example, a sheath-core type, an eccentric type, or an islands-in-sea type. When the high-modulus fiber is a composite fiber composed of two or more resin components, the high-modulus fibers may be fused to each other at the resin components constituting the surface thereof.

[0012]

The separator of the present invention preferably contains fine fibers having a fiber diameter of  $4\mu\text{m}$  or less, preferably  $3\mu\text{m}$  or less, more preferably  $2\mu\text{m}$  or less, as fibers forming the nonwoven fabric. This is because the nonwoven fabric has preferably a wide apparent total surface area of fibers per a unit area, to provide a separator having an excellent electrolyte-holding capacity.

For the fine fibers, it is preferable that a fiber diameter of each fine fiber is nearly identical to the other. This is because pores having a uniform pore diameter are formed by the fine fibers, and thus, the electrolyte is uniformly distributed. That is, a ratio  $(\sigma/d)$ , i.e., a quotient obtained by dividing a standard deviation ( $\sigma$ ) of a distribution of fiber diameters of the fine fibers by a mean value ( $d$ ) of fiber diameters of the fine fibers, is preferably 0.2 or less, more preferably 0.18 or less. If all of the fiber diameters of the fine



fibers are identical, a standard deviation ( $\sigma$ ) becomes zero, and the lower limit of the ratio ( $\sigma/d$ ) is zero.

The "mean value ( $d$ ) of fiber diameters of the fine fibers" is a value obtained by taking an electron micrograph of a sample of the separator, determining fiber diameters of 100 or more ( $n$ ) fine fibers on the electron micrograph, and taking an average of the 100 or more determined fiber diameters. The standard deviation ( $\sigma$ ) of the fine fibers can be calculated from each fiber diameter ( $\chi$ ) determined, using an equation:

$$\text{Standard deviation} = \{ (n\sum\chi^2 - (\sum\chi)^2) / n(n-1) \}^{1/2}$$

wherein  $n$  denotes the number of the determined fine fibers, and  $\chi$  denotes a fiber diameter of each fine fiber.

If the nonwoven fabric contains two or more groups of fine fibers having a fiber diameter of 4  $\mu\text{m}$  or less, preferably each group satisfies the above equation.

Further, it is preferable that each of the fine fibers has a diameter having a substantially same diameter in an axial direction of the fiber, so that the separator containing pores having a uniform pore diameter can be formed.

The fine fibers having nearly identical fiber diameters, or the fine fibers having a substantially same diameter in an axial direction of the fiber may be prepared, for example, by removing sea components from islands-in-sea type composite fibers obtained by a composite spinning method, such as a method for extruding and compositing island components into sea components under the condition that a spinning nozzle is controlled. It is generally difficult to obtain the fine fibers having nearly identical fiber diameters, or the fine fibers having a substantially same diameter in an axial direction of the fiber, by a

method called a mixing spinning method, that is, a method for mixing resins for island components and resins for sea components, then spinning the product to obtain islands-in-sea type fibers, and removing the sea components therefrom, or by a method called a melt-blowing method.

Preferably, the fine fibers are made from polyolefin resins, for example, polyethylene-based resins, such as, ultra-high-molecular-weight polyethylene, high-density polyethylene, middle-density polyethylene, low-density polyethylene, linear low-density polyethylene, or ethylene copolymers, polypropylene-based resin, such as polypropylene, or propylene copolymers, or polymethylpentene-based resin, such as polymethylpentene, methylpentene copolymers. Of these resins, polypropylene-based resin or polyethylene-based resin is preferable.

It is preferable that the fine fiber contains a resin component capable of participating in fusion (hereinafter sometimes referred to as a fusible component), because the fine fibers may be firmly fixed to avoid a dropping or raising of the fibers, when the fine fibers are fused by the fusible components.

If it is desirable to fuse the fine fibers, the fine fibers may be composed of only the fusible component of the above polyolefin-based resin, or two or more components, for example, the fusible component and a component (hereinafter sometimes referred to as a non-fusible component) having a melting point higher than that of the fusible component. It is more preferable that the fine fiber is composed of two or more components, for example, the fusible component and the non-fusible component, because a form or shape of the fine fiber may be maintained due to the presence of the non-fusible component, and thus,

interference to the intrinsic function of the fine fiber may not occur, i.e., interference to the formation of pores having a uniform pore diameter may not occur, when the fusible components are fused.

When the fine fiber is composed of two or more components, the fusible component preferably occupies a part of or all of the surface of the fine fiber, and thus can take part in the fusion. When the fine fiber is a composite fiber composed of two or more components, the cross-sectional shape is, for example, preferably a sheath-core type, an eccentric type, or an islands-in-sea type. The non-fusible component has a melting point higher than that of the fusible component, preferably by 10°C or more, more preferably by 20°C or more, so that the form or shape of the fine fibers can be maintained by the non-fusible component.

The fine fiber composed of two or more components, such as the fusible component and the non-fusible component, may be prepared by a method wherein a nozzle capable of producing the above-mentioned cross-sectional shape (such as a sheath-core type, an eccentric type, or an islands-in-sea type) is used as the nozzle for island components and spun to the islands-in-sea type fibers when spinning the islands-in-sea type fibers in a conventional composite spinning method, or a method wherein a resin mixture of two or more resin components is supplied to a nozzle for the island component and spun to the islands-in-sea type fibers when spinning the islands-in-sea type composite fibers in a conventional composite spinning method, and then the sea component is removed therefrom.

The term "melting point" as used herein means a temperature of a maximum value in a melting-endothermic

curve obtained by raising a temperature from room temperature at a rate of 10°C/min, using a differential scanning calorimeter. When there are two or more maximum values, the highest value is the melting point.

The above-mentioned advantageous effects can be easily achieved when the fine fibers account for 2 mass% or more (more preferably 5 mass% or more, most preferably 10 mass% or more) in the fibers forming the separator. The separator of the present invention preferably contains the above high-modulus fibers, to thus maintain moderate voids. Therefore, the amount of the fine fibers is preferably 80 mass% or less.

The fine fiber is preferably a short fiber having a fiber length of 30 mm or less and a high level of freedom, so that it is easily and uniformly dispersed. If the fine fibers or the island components in the islands-in-sea type fibers are press-bonded to each other when they are cut, the resulting fibers become like the fibrillated fibers. Therefore, it is preferable to use the fine fibers which are hard to press-bond to each other when cut, or the islands-in-sea type fibers containing the island components which are hard to press-bond to each other when cut.

As the fine fibers hard to press-bond or the islands-in-sea type fibers hard to press-bond, for example, high-crystalline fine fibers (or island components in the islands-in-sea type fibers) may be used. Specifically, it is preferable to contain polymethylpentene in the fine fibers (or island components in the islands-in-sea type fibers), or when containing polypropylene to use polypropylene having a melting point of 166°C or more, more preferably 168°C or more.

[0013]

The separator of the present invention may further contain fusible fibers, to enhance the strength of the nonwoven fabric.

The fusible component in the fusible fiber preferably has a melting point that does not affect the fibers such as the high-modulus fiber and/or the fine fibers other than the fusible fibers. For example, when the high-modulus fibers composed only of polypropylene-based resin and the fine fibers composed only of polypropylene-based resin are contained as the fibers other than the fusible fibers, the fusible fibers preferably contain polyethylene-based resins, such as, ultra-high-molecular-weight polyethylene, high-density polyethylene, middle-density polyethylene, low-density polyethylene, linear low-density polyethylene, or ethylene copolymers as the fusible component. Further, when the high-modulus fibers composed only of ultra-high-molecular-weight polyethylene and the fine fibers composed only of polypropylene-based resin are contained as the fibers other than the fusible fibers, the fusible fibers preferably contain polyethylene, such as, high-density polyethylene, middle-density polyethylene, low-density polyethylene, linear low-density polyethylene, or ethylene copolymers as the fusible component.

The fusible fiber may be composed of only the fusible component, or may contain the non-fusible component having a melting point higher than that of the fusible component in addition to the fusible component. When the fusible fibers are composite fibers composed of the fusible component and the non-fusible component as above, the strength of the nonwoven fabric can be enhanced. The cross-sectional shape of the composite fiber may be, for

example, a sheath-core type, an eccentric type, or an islands-in-sea type. Further, the non-fusible component is preferably composed of the resin having a melting point higher than that of the fusible component, preferably by 10°C or more, more preferably 20°C or more.

The fusible fibers are contained at an amount of preferably 20 mass% or more, more preferably 40 mass% or more in the fibers forming the separator, so that the strength of the separator can be enhanced. On the other hand, an amount of the fusible fibers is preferably 95 mass% or less because of the necessary existence of the high-modulus fibers or the fine fibers as above.

[0014]

The fibers, such as the high-modulus fibers, the fine fibers, or the fusible fibers, forming the separator of the present invention may be undrawn, but preferably are drawn because a good mechanical strength is thus obtained.

The fiber length of the fibers, such as the high-modulus fibers, the fine fibers, or the fusible fibers, forming the separator of the present invention is not particularly limited, but is preferably 0.5 to 30 mm, because a shorter fiber length brings a higher level of freedom of the fibers, and the fibers may be uniformly dispersed. More preferably, fibers cut to a length of 1 to 20 mm are used. The term "fiber length" as used herein means a value measured in accordance with JIS L1015 (a testing method for man-made staple fibers), the B method (an amended method for staple diagram).

[0015]

The nonwoven fabric forming the battery separator of the present invention has an apparent total surface area of fibers per a unit area of 20 m<sup>2</sup>/m<sup>2</sup> or more. Therefore, the

nonwoven fabric has an excellent electrolyte-holding capacity and can hold the electrolyte for a long term even if the thickness of the separator is 0.1 mm or less. The apparent total surface area of fibers per a unit area is preferably  $22 \text{ m}^2/\text{m}^2$  or more, more preferably  $25 \text{ m}^2/\text{m}^2$  or more.

The term "unit area" as used herein means a value obtained by placing a plate (the surface area of a single side =  $1 \text{ m}^2$ ) on the separator and cutting the separator in the direction of the thickness thereof and around the plate.

The term "apparent total surface area of fibers" as used herein means a sum of the surfaces area (except cross-sectional areas at both ends) of the fibers present in the above "unit area" under the condition that the fibers have not been fixed to each other. For example, when the separator contains the fusible fibers, they are fused. However, the "apparent total surface area" is calculated on the basis of the surface area (except cross-sectional areas at both ends) of the fusible fibers before fusing. If the plate (the surface area of a single side =  $1 \text{ m}^2$ ) cannot be placed on the separator, the apparent total surface area of fibers per  $1 \text{ m}^2$  can be calculated from the surface area of a single side of a plate which can be placed on the separator.

[0016]

The thickness of the nonwoven fabric used for the battery separator of the present invention is 0.1 mm or less, and thus it can be applied to the enhancement of the capacity of the battery. The term "thickness" as used herein means a thickness measured by an outside micrometer (0 to 25 mm) described in JIS B 7502:1994.

[0017]

In the nonwoven fabric used for the battery separator of the present invention, it is preferable that the fibers are fixed substantially only by a fusion of the fibers to each other. When the fibers are fixed only by the fusion, the arrangement of the fibers is not disturbed.

Therefore, a separator having a good uniformity, capable of effectively preventing a short circuit, capable of uniformly distributing the electrolyte, and having a lower inner resistance can be prepared. For example, when the fibers are fixed to each other by an entanglement, through holes are liable to be formed from the face side to the rear side of the separator, by an action for entangling the fibers to each other, by a fluid jet such as a water jet, or by needle, and thus, a short circuit is easily caused. On the contrary, if the fibers are fixed only by the fusion, the arrangement of the fibers is not disturbed, and thus, a short circuit is rarely caused.

When a nonwoven fabric is prepared, some fibers are entangled to each other. For example, a fiber web prepared by a card or a wet-laid method can maintain a shape thereof.

This means that the fibers are entangled more or less in the fiber web. However, the entanglement does not disturb the fibers arrangement in the fiber web as described above, and thus is not regarded as a substantial entanglement in the present invention. As above, the expression "substantially only by fusion of the fibers" as used herein means the condition wherein the fibers are fixed to each other only by fusion, after forming a fiber web. From another aspect, the above condition may be defined as the condition wherein the fibers, such as the high-modulus fibers, the fine fibers, or the fusible fibers, forming the separator (nonwoven fabric) are substantially two-



dimensionally arranged.

[0018]

As an indicator showing that the separator of the present invention has an excellent uniformity, there may be mentioned a "uniformity index". When the uniformity index is 0.15 or less, the separator has an excellent uniformity, is capable of effectively preventing a short circuit, and can uniformly hold the electrolyte. Preferably, the uniformity index is 0.10 or less.

The "uniformity index" is calculated by a method disclosed in Japanese Patent Application No. 11-152139. Specifically, the "uniformity index" is calculated by the following method wherein:

- (1) Brightness information is obtained by irradiating a sample (separator) with light from an illuminant, and receiving a reflected light from a predetermined region of the sample at a light-receptor element;
- (2) Four divisional patterns having an image size of 3 mm x 3 mm, 6 mm x 6 mm, 12 mm x 12 mm, and 24 mm x 24 mm are obtained by equally dividing the predetermined region of the sample;
- (3) A brightness value of each zone in the resulting divisional patterns is calculated on the basis of the brightness information;
- (4) An average brightness (X) of each divisional pattern is calculated on the basis of the brightness value of each zone;
- (5) A standard deviation ( $\sigma$ ) of each divisional pattern is calculated;
- (6) A coefficient of variation (CV) of each divisional pattern is calculated from an equation:

$$\text{Coefficient of Variation (CV)} = (\sigma/X) \times 100$$

wherein  $\sigma$  denotes a standard deviation of each divisional pattern, and  $X$  denotes an average brightness of each divisional pattern;

(7) A group of coordinates having an  $X$  axis of a logarithm of each image size and a  $Y$  axis of a coefficient of variation of the corresponding image size is made, and regressed to a primary line by a method of least squares to calculate a slope thereof. An absolute value of the resulting slope is a uniformity index.

[0019]

In the nonwoven fabric (separator) of the present invention, a maximum pore size is preferably 40  $\mu\text{m}$  or less, because the uniformity of the nonwoven fabric thus becomes excellent, and if the separator of the nonwoven fabric is strongly pressed against the electrodes, loose powdery active materials hardly invade the inner voids in the separator, and a short circuit is effectively prevented. The maximum pore size is more preferably 35  $\mu\text{m}$  or less, most preferably 30  $\mu\text{m}$  or less. The term "maximum pore size" as used herein means a value measured in accordance with a bubble point method, using a porometer (Coulter Electronics Ltd.).

[0020]

In the separator (nonwoven fabric) of the present invention, the maximum pore size of the pores in the nonwoven fabric is preferably 2 times or less, more preferably 1.9 times or less a mean flow pore size. Within the above range, the nonwoven fabric has a narrow distribution of the pore size, and an electrolyte can be uniformly dispersed, to thereby assemble a battery having a low internal resistance. Ideally the maximum pore size is 1 times the mean flow pore size, namely, all of the pores

have the same size. The term "mean flow pore size" as used herein means a value defined in ASTM-F316, and measured, for example, in accordance with a mean-flow point method, using a porometer (Coulter Electronics Ltd.).

[0021]

The void rate of the nonwoven fabric (separator) of the present invention is preferably 45 to 65 %, more preferably 50 to 60 % so that the internal resistance and the inner pressure are lowered, and the electrolyte-holding capacity is enhanced.

The void rate (P) is calculated by an equation:

$$\text{Void rate (P)} = \{1 - W / (T \times d)\} \times 100$$

wherein W denotes a surface density ( $\text{g/m}^2$ ), T denotes a thickness ( $\mu\text{m}$ ) of the nonwoven fabric (or a separator), and d denotes a density ( $\text{g/cm}^3$ ) of the resin (for example, a fiber) forming the nonwoven fabric. When the nonwoven fabric contains two or more kinds of resins, the density of the constituent resins is an average of masses of the constituent resins. For example, when there are a mass% of a resin A having a density  $d_1$ , and b mass% of a resin B having a density  $d_2$ , the density of the constituent resins is calculated from an equation:

$$d = d_1 \times a / 100 + d_2 \times b / 100.$$

[0022]

It is preferable that a tensile strength in at least one direction of the separator (nonwoven fabric) of the present invention is 20 N/5 cm width or more, because an electrode group can be thus assembled without breakage, and a battery can be assembled with a good yield. The tensile strength is more preferably 30 N/5 cm width or more, most preferably 40 N/5 cm width or more.

The "tensile strength" means a power required to

break a separator when a sample cut to a 5 cm width is set between chucks (distance between the chucks = 10 cm) of a tensile tester (TENSILON UTM-III-100; manufactured by ORIENTEC, Co.), and the sample is pulled at a pulling rate of 300 mm/min.

[0023]

A resistance to needle-penetration of the separator of the present invention is preferably 500 gf or more. If the resistance to needle-penetration is less than 500 gf, the fibers forming the nonwoven fabric are separated by a flash from the electrode, and a short circuit is easily caused when a group of electrodes is formed. The resistance to needle-penetration is more preferably 600 gf or more, most preferably 700 gf or more.

The resistance to needle-penetration is measured as follows:

A separator sample is mounted on a supporting cylinder with a through hole (inner diameter = 11 mm) having a circular sectional shape, so that the through hole is covered with the sample. Further, a fixing cylinder with a through hole (inner diameter = 11 mm) having a circular sectional shape is mounted on the sample, so that the center of the fixing cylinder conforms to the center of the through hole of the supporting cylinder, to thereby fix the sample. Then, a needle (curvature radius = 0.5 mm at the tip; diameter = 1 mm, a length projected from a jig = 2 cm) set on a handy-type compression tester (KES-G5; manufactured by KATO TECH Co., Ltd.) is thrust perpendicularly into the sample at a rate of 0.01 cm/s, and a force required to pierce the sample with the needle is measured. The force required gives the resistance to needle-penetration of the sample.

[0024]

The surface density of the separator of the present invention is preferably 5 to 55 g/m<sup>2</sup>, more preferably 10 to 40 g/m<sup>2</sup>.

[0025]

It is preferable to introduce one or more oxygen- and/or sulfur-containing functional groups such as sulfonic acid group, sulfate group, sulfofluoride group, carboxyl group, or carbonyl group, onto the surfaces of the fibers constituting the separator of the present invention; to graft-polymerize one or more hydrophilic monomers on the surfaces; to apply one or more surface-active agents to the surfaces; or to apply one or more hydrophilic resin to the surfaces; so that an affinity thereof to an electrolyte is imparted or enhanced.

[0026]

The separator of the present invention can be used, for example, as a separator of a primary battery, such as an alkaline-manganese battery, a mercury battery, a silver oxide battery, an air battery, or the like, or a secondary battery, such as a nickel-cadmium battery, silver-zinc battery, silver-cadmium battery, nickel-zinc battery, nickel-hydrogen battery, or the like.

[0027]

The separator (nonwoven fabric) of the present invention may be prepared, for example, by a following method:

A surface density (g/m<sup>2</sup>) is first designed. Then, on the basis of the designed surface density, a fiber combination is determined so that an apparent total surface area of fibers per a unit area of a desired nonwoven fabric becomes 20 m<sup>2</sup>/m<sup>2</sup> or more. In general, the above requirement

is easily satisfied when the fine fibers are contained in a large amount. Further, if non-fibrillated fibers are used as the fibers, a separator having a good uniformity and capable of uniformly holding an electrolyte can be easily prepared. It is preferable to select substantially only polyolefin-based fibers having an excellent resistance to an electrolyte, i.e., preferably the above-mentioned high-modulus fibers, the above-mentioned fine fibers, and the above-mentioned fusible fibers.

[0028]

Thereafter, a fiber web is formed from the selected fibers. The method for preparing the fiber web is not particularly limited, but the fiber web may be prepared by a dry-laid method, such as a carding method, an air-laid method, a spun-bonding method, or a melt-blown method, or a wet-laid method. Of these methods, the wet-laid method is preferable, because the nonwoven fabric having a property of a uniform dispersal of fibers and an easiness of uniformly holding an electrolyte may be easily prepared. As the wet-laid method, there may be mentioned conventional methods, such as a flat long-wire type, an inclined short-wire type, a cylindrical type, or a long-wire/cylindrical type.

[0029]

Then, the fibers constituting the fiber web may be fixed to each other to obtain the separator of the present invention. The fixation of the fibers is preferably carried out only by fusion. When the fibers are fixed only by fusion, the arrangement of the fibers is not disturbed. Therefore, a separator having a good uniformity, capable of effectively preventing a short circuit, capable of uniformly distributing the electrolyte, and having a lower

inner resistance can be easily prepared. Therefore, the fiber web preferably contains the fusible fibers as the constituent fibers.

[0030]

The fusing step of the fiber web may be carried out without or with an applied pressure. Alternatively, the fusible components may be melted without an applied pressure, and then (preferably immediately thereafter) the web may be pressed. A heating temperature in each case is preferably from a softening point of the fusible component of the fusible fibers to a temperature higher than a melting point of the fusible component of the fusible fibers by 30°C. It is preferable to adjust a pressure when applied so that the void rate of the resulting nonwoven fabric becomes 45 to 65 %, and the tensile strength of the resulting nonwoven fabric becomes 20 N/5 cm width or more in at least one direction.

The term "softening point" as used herein means a temperature of a starting point in a melting-endothermic curve obtained by raising a temperature from room temperature at a rate of 10°C/min, using a differential scanning calorimeter.

[0031]

The separator of the present invention can be used to enhance the battery capacity because of the thinness thereof. Therefore, if the thickness of the fiber web after fusing is more than 0.1 mm, the thickness is adjusted to 0.1 mm or less by, for example, passing the web through a pair of rolls.

[0032]

The separator (nonwoven fabric) having a uniformity index of 0.15 or less, a maximum pore size of 40  $\mu\text{m}$  or less,

and/or a maximum pore size that is 2 times or less the mean flow pore size may be prepared by a method wherein the fine fibers are used, a method wherein the non-fibrillated fibers are used, a method wherein short fibers having a fiber length of 1 to 20 mm are used, a method wherein the fiber web is produced by the wet-laid method, or a method wherein the fibers are fixed only by fusion without an entanglement, or by a combination of two or more methods as above.

[0033]

The separator (nonwoven fabric) having a void rate of 45 to 65 % may be prepared by a method wherein an amount of the fine fibers used is reduced, a method wherein an amount of the fibers used is reduced, or a method wherein a pressure applied when fusing is adjusted to increase the thickness, or by a combination of two or more methods as above.

[0034]

The separator (nonwoven fabric) of the present invention having a tensile strength of 20 N/5 cm width or more in at least one direction may be prepared by a method wherein the fibers are oriented into one direction by adjusting an amount of a flow of slurry and a moving rate of a net taking up the fibers, a method wherein a degree of fusion is increased, or a method wherein the fibers having a long fiber length are used, or by a combination of two or more methods as above.

[0035]

The separator of the present invention having a resistance to needle-penetration of 500 gf width or more may be prepared by a method wherein the high-modulus fibers having a high Young's modulus are used, a method wherein an



amount of high-modulus fibers used is increased, a method wherein the high-modulus fibers are uniformly dispersed, a method wherein a tight fusion by the fusible fibers is carried out, a method wherein the fusible fibers are melted and immediately thereafter pressed to cause a fusion, or by a combination of two or more methods as above.

[0036]

The separator prepared by the above method has a substantially unilayered structure, an apparent total surface area of fibers per a unit area of  $20 \text{ m}^2/\text{m}^2$  or more, and a thickness of 0.1 mm or less. Therefore, a battery capable of uniformly holding the electrolyte throughout the separator, and having a low inner pressure and a high capacity can be assembled. Further, a battery having a good electrolyte-holding capacity, particularly, a long-term electrolyte-holding capacity, and thus a long-term lifetime, can be assembled.

[0037]

In a preferred embodiment of the separator (nonwoven fabric) of the present invention, the fibers are composed only of the polyolefin-based fibers, to obtain an excellent resistance to alkalis. Therefore, it is preferable to carry out a treatment for imparting a hydrophilic property, to enhance the electrolyte-holding capacity. The treatment for imparting a hydrophilic property may be, for example, a sulfonating treatment, a treatment with fluorine gas, a graft polymerization treatment with vinyl monomers, a treatment with a surface-active agent, a discharging treatment, or a treatment to adhere hydrophilic resins.

[0038]

The sulfonating treatment contains, for example, but is not limited to, a method for introducing sulfonic acid

groups into the nonwoven fabric by dipping the nonwoven fabric in a solution of fuming sulfuric acid, sulfuric acid, sulfur trioxide, chlorosulfuric acid, or sulfonyl chloride, or a method for introducing sulfonic acid groups into the nonwoven fabric by subjecting a discharging treatment to the nonwoven fabric in the presence of sulfur monoxide gas, sulfur dioxide gas, sulfur trioxide gas or the like.

[0039]

The treatment with fluorine gas is not limited. For example, a hydrophilic property can be imparted to the fiber surfaces of the nonwoven fabric by exposing the nonwoven fabric to a gas mixture of fluorine gas diluted with an inactive gas (such as nitrogen or argon) and at least one gas selected from a group consisting of oxygen, carbon dioxide and sulfur dioxide gases. A permanent hydrophilic property can be more effectively imparted by adhering sulfur dioxide gas to the nonwoven fabric, and then bringing the nonwoven fabric into contact with fluorine gas.

[0040]

Examples of the vinyl monomer which may be used in the graft polymerization with vinyl monomers are acrylic acid, methacrylic acid, acrylate, methacrylate, vinyl pyridine, vinyl pyrrolidone, or styrene. When styrene is graft polymerized, it is preferable to carry out a sulfonation, to impart an affinity with an electrolyte. Of these monomers, acrylic acid has a good affinity with an electrolyte and may be preferably used.

A method for polymerizing the vinyl monomers is, for example, a method for dipping the nonwoven fabric in a solution containing the vinyl monomers and an initiator, and heating; a method for coating the nonwoven fabric with vinyl monomers and applying radiation; a method for

applying radiation to the nonwoven fabric and then bringing the nonwoven fabric into contact with the vinyl monomers; a method for impregnating the nonwoven fabric with a solution containing vinyl monomers and a sensitizing agent, and applying ultraviolet rays. The graft polymerization can be effectively carried out by modifying the surface of fibers with ultraviolet radiation, a corona discharge or a plasma discharge before bringing the nonwoven fabric into contact with the vinyl monomer solution, to enhance the affinity thereof with the vinyl monomer solution.

[0041]

The treatment with a surface-active agent may be carried out, for example, by coating or spraying a solution of an anionic surface-active agent (such as an alkali metal salt of a higher fatty acid, alkyl sulfonate, or a salt of sulfosuccinate) or a nonionic surface-active agent (such as polyoxyethylene alkyl ether, or polyoxyethylene alkylphenol ether) to the nonwoven fabric, or dipping the nonwoven fabric in the solution.

[0042]

As the discharging treatment, there may be mentioned, for example, treatments with a corona discharge, plasma, glow discharge, surface discharge, or electron rays. Of the discharging treatments, a method comprising the steps of placing the nonwoven fabric between a pair of electrodes carrying a dielectric layer respectively in air under an atmospheric pressure, so that the nonwoven fabric is brought into contact with both dielectric layers, and then applying an alternating current voltage between the electrodes to thereby induce an electric discharge in internal voids contained in the nonwoven fabric, can be preferably conducted. This is because not only the outer

surfaces but also the insides of the nonwoven fabric can be thus treated; and therefore, a battery having the separator with an excellent electrolyte-holding capacity can be produced from the resulting nonwoven fabric.

[0043]

The treatment to apply hydrophilic resins can be carried out by adhering hydrophilic resins, such as carboxymethyl cellulose, polyvinyl alcohol, polyvinyl alcohol which is cross-linkable, or polyacrylic acid, to the nonwoven fabric. The hydrophilic resins may be adhered to the nonwoven fabric by coating or spraying the nonwoven fabric with a solution prepared by dissolving or dispersing the hydrophilic resins in an appropriate solvent, or dipping the nonwoven fabric in the solution, and then drying. The amount of the hydrophilic resins adhered is preferably 0.3 to 5 mass% with respect to an amount of the whole separator, so as not to affect the air permeability.

The cross-linkable polyvinyl alcohol is, for example, polyvinyl alcohol substituted by a photosensitive group at a part of hydroxyl groups, particularly polyvinyl alcohol having styryl pyridinium, styryl quinolinium, or styryl benzthiazolinium groups as the photosensitive group. The cross-linking of the cross-linkable polyvinyl alcohols can be carried out by adhering the cross-linkable polyvinyl alcohols to the nonwoven fabric as in the case of other hydrophilic resins and irradiating the cross-linkable polyvinyl alcohols with light. The polyvinyl alcohol substituted by a photosensitive group at a part of hydroxy groups has an excellent resistance to alkalis and contains many hydroxyl groups enabling a formation of chelates with ions, and thus can form chelates with ions before the ions are deposited on electrodes in the form of branches, during

charging and/or discharging, to thereby effectively prevent a short circuit between the electrodes.

[0044]

The present invention now will be further illustrated by, but is by no means limited to, the following Examples.

[0045]

[EXAMPLES]

(Example 1)

As the islands-in-sea type fibers, fibers (fineness = 1.65 dtex, fiber length = 2 mm) having 25 island components of polypropylene in a sea component of poly-L-lactic acid (hereinafter referred to as "PLLA") were prepared by a composite spinning method.

Then, the islands-in-sea type fibers were dipped in a bath (temperature = 80°C) of a 10 mass% aqueous solution of sodium hydroxide for 30 minutes, and the sea component, PLLA, in the islands-in-sea type composite fibers was extracted and removed to obtain polypropylene fine fibers (fiber diameter = 2 $\mu$ m,  $\rho/d$  = 0.083, melting point = 172°C, fiber length = 2 mm, density = 0.91 g/cm<sup>3</sup>). The resulting polypropylene fine fibers were drawn and not fibrillated. Each of fibers had substantially same diameter in an axial direction thereof.

Further, as the fusible fibers, sheath-core type composite fibers (fineness = 0.8 dtex, fiber length = 5 mm, mass ratio of the core component and the sheath component = 1:1, non-fibrillated, drawn) having a core component (non-fusible component) of polypropylene (melting point = 168°C, density = 0.91 g/cm<sup>3</sup>), and a sheath component (fusible component) of high density polyethylene (melting point = 135°C, density = 0.96 g/cm<sup>3</sup>) was prepared.

Furthermore, as the high-modulus fibers, fibers (Young's modulus = 90 cN/dtex, fineness = 1.3 dtex, fiber length = 10 mm, density = 0.91 g/cm<sup>3</sup>, non-fibrillated, drawn) of high-crystalline polypropylene was prepared.

Then, 20 mass% of the polypropylene fine fibers, 50 mass% of the sheath-core type composite fibers, and 30 mass% of the polypropylene high-modulus fibers were mixed, and a fiber web was formed by a wet-laid method (Horizontal Fourdrinier method) from a dispersed slurry.

Then, the fiber web was allowed to stand in a dryer with an internal air circulation at 135°C for 3 minutes, to dry the fiber web and thermally fuse the sheath components (high density polyethylene) of the sheath-core type composite fibers, and thus form a fused nonwoven fabric.

Thereafter, the fused nonwoven fabric was dipped in a solution of fuming sulfuric acid (15%SO<sub>3</sub>) for 2 minutes at 60°C, thoroughly washed with water, and dried to obtain a sulfonated nonwoven fabric having sulfonic acid groups introduced on the fiber surfaces.

Then, the sulfonated nonwoven fabric was calendared to produce a unilayered-structural separator (surface density = 40 g/m<sup>2</sup>, thickness = 0.10 mm, apparent total surface area = 29.8 m<sup>2</sup>/m<sup>2</sup>, the fibers being substantially two-dimensionally arranged).

[0046]

(Example 2)

As the islands-in-sea type fibers, fibers (fineness = 1.65 dtex, fiber length = 2 mm) having 25 island components of a mixture of polypropylene and high density polyethylene in a sea component of PLLA were prepared by a composite spinning method.

Then, the islands-in-sea type fibers were dipped in

a bath (temperature = 80°C) of a 10 mass% aqueous solution of sodium hydroxide for 30 minutes, and the sea component, PLLA, in the islands-in-sea type composite fibers was extracted and removed to obtain polypropylene-high density polyethylene mixed fine fibers (melting point of high density polyethylene = 135°C, fiber diameter = 2  $\mu$ m,  $\rho/d$  = 0.09, fiber length = 2 mm, density of polypropylene = 0.91 g/cm<sup>3</sup>, density of high density polyethylene = 0.96 g/cm<sup>3</sup>, mixing ratio of polypropylene and high density polyethylene = 1:1, non-fibrillated, drawn, diameter being substantially the same in an axial direction of each fiber).

Further, the fusible fibers (sheath-core type composite fibers) and the high-modulus fibers were prepared as in Example 1.

Then, 20 mass% of the polypropylene fine fibers, 50 mass% of sheath-core type composite fibers, and 30 mass% of polypropylene high-modulus fibers were mixed, and the procedure of Example 1 was repeated to produce a unilayered-structural separator (surface density = 40 g/m<sup>2</sup>, thickness = 0.10 mm, apparent total surface area = 29.8 m<sup>2</sup>/m<sup>2</sup>, the fibers being substantially two-dimensionally arranged) wherein the high density polyethylene components of the polypropylene-high density polyethylene mixed fine fibers were fused, and sulfonic acid groups were introduced onto the fiber surfaces.

[0047]

(Comparative Example 1)

The fusible fibers (sheath-core type composite fibers) and the high-modulus fibers were prepared as in Example 1.

Then, 65 mass% of the sheath-core type composite fibers and 35 mass% of polypropylene high-modulus fibers

were mixed, and a fiber web was formed by a wet-laid method (Horizontal Fourdrinier method) from the dispersed slurry.

Then, the fiber web was allowed to stand in a dryer with an internal air circulation at 135°C for 3 minutes to dry the fiber web and thermally fuse the sheath components (high density polyethylene) of the sheath-core type composite fibers, and thus form a fused nonwoven fabric (surface density = 32 g/m<sup>2</sup>).

Further, two polypropylene melt-blown nonwoven fabrics having an average fiber diameter of 2 μm and a surface density of 4 g/m<sup>2</sup> were prepared.

Then, one of the melt-blown nonwoven fabrics was placed on the fused nonwoven fabric, and the whole was passed through heated rolls at 135°C to perform a thermal bonding by the sheath components (high density polyethylene) in the sheath-core type composite fibers of the fused nonwoven fabric, and thereby form a one-side-fused nonwoven fabric.

Thereafter, the other melt-blown nonwoven fabric was placed on the non-fused surface of the resulting one-side-fused nonwoven fabric, and the whole was passed through heated rolls at 135°C to perform a thermal bonding by the sheath components (high density polyethylene) in the sheath-core type composite fibers of the fused nonwoven fabric and thereby form a both-side-fused nonwoven fabric.

Then, as in Example 1, sulfonic acid groups were introduced to the resulting both-side-fused nonwoven fabric, and the sulfonated fabric was calendared to produce a trilayered-structural separator (surface density = 40 g/m<sup>2</sup>, thickness = 0.10 mm, apparent total surface area = 29.8 m<sup>2</sup>/m<sup>2</sup>).

[0048]



(Comparative Example 2)

The fusible fibers (sheath-core type composite fibers) and the high-modulus fibers were prepared as in Example 1.

Then, 70 mass% of the sheath-core type composite fibers and 30 mass% of the polypropylene high-modulus fibers were mixed, and a fiber web was formed by a wet-laid method (Horizontal Fourdrinier method) from the dispersed slurry.

Then, the fiber web was allowed to stand in a dryer with an internal air circulation at 135°C for 3 minutes to dry the fiber web and thermally fuse the sheath component (high density polyethylene) of the sheath-core type composite fibers, and thus form a fused nonwoven fabric.

Then, as in Example 1, sulfonic acid groups were introduced to the resulting fused nonwoven fabric, and the sulfonated fabric was calendared to produce a unilayered-structural separator (surface density = 40 g/m<sup>2</sup>, thickness = 0.10 mm, apparent total surface area = 15 m<sup>2</sup>/m<sup>2</sup>).

[0049]

(Measurement of uniformity index)

The uniformity index of each separator was determined by the following procedures:

- (1) Brightness information was obtained by irradiating a sample (fiber sheet) with light from an illuminant, and receiving a reflected light from a predetermined region of the sample at a light-receptor element;
- (2) Four divisional patterns having an image size of 3 mm x 3 mm, 6 mm x 6 mm, 12 mm x 12 mm, and 24 mm x 24 mm were obtained by equally dividing the predetermined region of the sample;
- (3) A brightness value of each zone in the resulting

divisional patterns was calculated on the basis of the brightness information:

(4) An average brightness ( $X$ ) of each divisional pattern was calculated on the basis of the brightness value of each zone.

(5) A standard deviation ( $\sigma$ ) of each divisional pattern was calculated.

(6) A coefficient of variation (CV) of each divisional pattern was calculated from an equation:

$$\text{Coefficient of Variation (CV)} = (\sigma/X) \times 100$$

wherein  $\sigma$  denotes a standard deviation of each divisional pattern, and  $X$  denotes an average brightness of each divisional pattern:

(7) A group of coordinates having an X axis of a logarithm of each image size and a Y axis of a coefficient of variation of the corresponding image size was made, and regressed to a primary line by a method of least squares to calculate a slope thereof. An absolute value of the resulting slope was a uniformity index. A smaller uniformity index indicates that the fibers are more uniformly dispersed.

The results are shown in Table 1. As apparent from Table 1, the separators of the present invention have a small uniformity index of 0.09 or less, and an excellent uniformity. Therefore, it is expected that the separators of the present invention can effectively prevent a short circuit, and uniformly hold the electrolyte.

[0050]

[Table 1]

	Example 1	Example 2	Comparative Example 1	Comparative Example 2
Surface density (g/m <sup>2</sup> )	40	40	40	40
Thickness (mm)	0.1	0.1	0.1	0.1
Apparent total surface area (m <sup>2</sup> /m <sup>2</sup> )	29.8	29.8	29.8	15
Uniformity index	0.08	0.09	0.12	0.14
Maximum pore Size ( $\mu$ m)	20.5	21.0	26.9	47.1
Ratio (#)	1.7	1.8	2.0	2.2
Void rate (%)	56.8	56.8	56.8	57.0
Tensile strength (N/5cm width)	73	82	96	102
Resistance to penetration (gf)	760	772	525	552
Electrical resistance ( $\Omega$ )	0.2	0.23	0.61	0.26
Holding capacity of liquid under pressure (%)	10.9	9.8	8.9	6.5

(#): Ratio = (maximum pore size )/(mean flow pore size)

[0051]

(Measurement of maximum pore size)

The maximum pore size of each of the separators was measured in accordance with a bubble point method using a porometer (Coulter Electronics Ltd.). The results are shown in Table 1. As apparent from Table 1, the separators of the present invention have a small maximum pore size of 21  $\mu\text{m}$  or less. Therefore, it is expected that the separators of the present invention have an excellent uniformity and loose powdery active materials can be prevented from moving to the other electrode.

[0052]

(Measurement of ratio (maximum pore size/mean flow pore size))

The mean flow pore size of each of the separators was measured in accordance with a mean-flow point method, using a porometer (Coulter Electronics Ltd.).

Then, the ratio (maximum pore size/mean flow pore size) was calculated by dividing the maximum pore size obtained as described above by the mean flow pore size. The results are shown in Table 1. As apparent from Table 1, the separators of the present invention have a small ratio (maximum pore size/mean flow pore size). Therefore, it is expected that the electrolyte can be uniformly dispersed in the separators of the present invention and a battery having a low inner resistance can be assembled.

[0053]

(Measurement of void rate)

A surface density (W) and a thickness (T) of each of the separators were measured.

Then, a density (d) of the constituent fibers of each of the separators was calculated from the density and

the mass ratio of each of the constituent fibers.

Thereafter, the void rate (P) is calculated by an equation:

$$\text{Void rate (P)} = \{1 - W / (T \times d)\} \times 100$$

The results are shown in Table 1. As apparent from Table 1, it is expected that the separators of the present invention have a low inner resistance and inner pressure, and a high electrolyte-holding capacity.

[0054]

(Measurement of lengthwise tensile strength)

Each separator sample cut to 5 cm width was set between chucks (distance between the chucks = 10 cm) of a tensile tester (TENSILON UTM-III-100; manufactured by ORIENTEC, Co.), the sample was pulled in the lengthwise direction at a pulling rate of 300 mm/min, and a power required to break the separator was measured as the lengthwise tensile strength. The results are shown in Table 1. As apparent from Table 1, it is expected that the separators of the present invention are not broken when a group of electrodes is formed, and therefore, a battery can be assembled in a good yield.

[0055]

(Resistance to needle-penetration)

Each separator sample was mounted on a supporting cylinder with a through hole (inner diameter = 11 mm) having a circular sectional shape so that the through hole was covered with the separator sample. Further, a fixing cylinder with a through hole (inner diameter = 11 mm) having a circular sectional shape was mounted on the sample so that the center of the fixing cylinder conformed to the center of the through hole of the supporting cylinder, to thereby fix the sample. Then, a needle (curvature radius =

0.5 mm at the tip; diameter = 1 mm, a length projected from a jig = 2cm) set on a handy-type compression tester (KES-G5; manufactured by KATO TECH Co., Ltd.) was thrust perpendicularly into the sample at a rate of 0.01 cm/s, and a force required to pierce the sample with the needle was measured. The required force was taken as the resistance to needle-penetration. The results are shown in Table 1. As apparent from Table 1, it is expected that the fibers constituting the separators of the present invention are not divided by a flash from the electrode when a group of electrodes is formed, and therefore, a short circuit is not easily caused.

[0056]

(Measurement of electrical resistance)

Each separator was cut to samples of 35 mm x 35 mm.

Then, an aqueous potassium hydroxide solution having a specific gravity of 1.3 (20°C) was adsorbed into each sample at a mass the same as that of the sample. The sample was put between two nickel plates (35 mm x 35 mm), and an electrical resistance was measured under a pressure of 5 kgf. The results are shown in Table 1. As apparent from Table 1, the separators of the present invention have a low electrical resistance, and can be applied to being an enhancement of the battery capacity.

[0057]

(Measurement of holding capacity of liquid under pressure)

Each separator was cut to samples of 30 mm x 30 mm.

Each of the samples was allowed to stand at 20°C and a relative humidity of 65% to a moisture equilibrium, and then a mass ( $M_0$ ) thereof was measured.

Then, each of the samples was dipped in an aqueous potassium hydroxide solution having a specific gravity of

1.3 (20°C) for 1 hour, to replace air in the sample with the aqueous potassium hydroxide solution, and the aqueous potassium hydroxide solution was maintained in the sample.

Thereafter, each of the samples was put between two sets of three filter papers (diameter = 30 mm), and a pressure of 5.7 Mpa was applied for 30 seconds by a pressure pump, and a mass ( $M_1$ ) thereof was measured.

A holding capacity of liquid under pressure (HCUP) was calculated by the following equation:

$$\text{HCUP}(\%) = \{(M_1 - M_0) / M_0\} \times 100$$

The measurements were conducted 4 times for each sample, and an average was calculated as the holding capacity of liquid under pressure. The results are shown in Table 1. As apparent from Table 1, it is expected that the separators of the present invention have an excellent electrolyte-holding capacity, and a battery having a long lifetime can be assembled.

[0058]

[Effects of the Invention]

The battery separator of the present invention has a substantially unilayered structure, and thus can uniformly hold the electrolyte. Therefore, a battery having a low inner pressure and a high capacity can be assembled therefrom. Further, the battery separator of the present invention has an apparent total surface area of fibers per a unit area of 20 m<sup>2</sup>/m<sup>2</sup> or more, even though the thickness is 0.1 mm or less. Therefore, a battery having a good electrolyte-holding capacity, particularly a long-term electrolyte-holding capacity, and thus a long-term lifetime, can be assembled.

[DOCUMENT NAME] Abstract

[ABSTRACT]

[OBJECT] A thin battery separator enabling an enhancement of the capacity of the battery is provided.

[MEANS FOR SOLUTION] The separator for an alkaline battery of the present invention is characterized by consisting of a nonwoven fabric having a substantially unilayered structure, wherein an apparent total surface area of fibers per a unit area of the nonwoven fabric is  $20 \text{ m}^2/\text{m}^2$  or more, and a thickness of the nonwoven fabric is 0.1 mm or less.

[SELECTED DRAWINGS] None